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Acute Toxicities of Selected Hydrometallurgical Chemicals to Fish

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Ministry
of the
Environment

Ontario

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ACUTE TOXICITIES OF SELECTED
HYDROMETALLURGICAL CHEMICALS TO FISH

by

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SUMMARY

As part of its regular bioassay program, the Toxicity Unit tested thirteen hydrometallurgical chemicals that are presently used in Ontario for extractions of rare metals. The testing of these compounds was requested by the Ministry of the Environment Pollution Control Branch in order to establish the maximum allowable residual discharge levels.

Fathead minnows (*Pimephales promelas*) and guppies (*Poecilia reticulata*) were exposed to differing concentrations of the chemicals, and median lethal concentrations (LC_{50}) were obtained. The LC_{50} values of the compounds tested ranged from 140.0 µg/liter to 173.0 mg/liter. Under the test conditions fathead minnows were significantly more sensitive than the guppies ($p<.01$). Recommendations are made for allowable reagent discharges.

INTRODUCTION

At the request of the Ministry of the Environment Pollution Control Branch, acute toxicity values were determined for 13 mining reagents by establishing median lethal concentrations (LC_{50}) for fathead minnows (Pimephales promelas) and guppies (Poecilia reticulata).

The chemicals investigated in this study are employed primarily in hydrometallurgical extractions of rare metals in Ontario (Table #1). Although present usage statistics are unavailable, the quantities used are relatively small when considering the magnitude of Ontario mining operations as a whole. However, usage of the above reagents is to be expanded greatly in the near future by Rio-Algom Mines uranium recovery operations at Blind River. Anticipated residual discharges are not expected to exceed the 10.0 ppm level in the process effluents (Hawley 1976). At present no specific Provincial or Federal discharge regulations exist for the materials tested.

It is hoped that the results of this study will facilitate toxicity estimating of the different mine-mill process effluents, and enable the field personnel to establish priorities for more rigorous bioassay testing.

METHODS AND MATERIALS

Cylindrical glass jars of 19-liter capacity, 27 cm in diameter and 48 cm high were used in all minnow bioassays, whereas jars 24 cm in diameter and 28 cm high were used in all guppy tests.

Dechlorinated municipal water of approximately 137 ppm hardness as ($CaCO_3$) was used for all bioassays (Table 2).

Dissolved oxygen, temperature and pH determinations were made at the beginning of each test and every 48 hours thereafter throughout the exposure period.

Two fish species were used in the study. Guppies (Poecilia reticulata) were drawn from existing stocks cultured in our laboratory, while the fathead minnows (Pimephales promelas) were obtained from a hardwater pond in Vaughan Township. All fathead minnows were subjected to a single acriflavine (4 ppm) treatment shortly after capture and introduction into the holding tanks. Since the testing conditions were identical to both the culture and holding conditions for both species, no acclimation of the fish was required prior to testing. All fish stocks met the required acclimation criteria as outlined by Sprague (1969), and all were starved 48 hours before testing. The guppies used in the tests had a mean length of 1.64 ± .26 cm, and a mean weight of .05 grams, while the mean length and weight of the fathead minnows were 4.91 ± .54 cm and 1.11 grams respectively. Preliminary range tests were conducted with laboratory-raised guppies, while guppies and fathead minnows were used in full-scale exposures to obtain LC_{50} values for each test compound. Range tests utilized three guppies per concentration, whereas subsequent full-scale bioassays consisted of duplicate test concentrations, each with five fish.

In order to standardize the preparation of the toxicant, a 2-liter 0.1% stock solution was prepared and mixed by a Sonifier Cell Disruptor (Model #W185) for four minutes at the control setting #8, (10-watt output). In order to minimize evaporation of the volatile components, a water bath was employed during the mixing process to cool the stock solution.

Fish mortalities were recorded at twelve hour intervals, although inspection and removal of dead fish was more frequent. An estimate of the LC_{50} was obtained for each bioassay by plotting the percent survival versus the log concentration of the toxicant. Exposure concentrations were chosen from a progressive bisection of a logarithmic series (Doudoroff 1951).

White's (1952) non-parametric test (an extension of the Wilcoxon ranking test) was used to compare toxicity responses of the two species tested, whereas the "t" distribution was used to test the significance of differences in bioassay loading rates.

All bioassays were conducted without artificial aeration and at room temperature (20 ± 1°C).

RESULTS AND DISCUSSION

With the exception of LIX 64 and Adogen 283, median lethal concentrations were established for all toxicants tested (Table 3). The above two chemicals produced a layer of oily residue that made guppy testing difficult. Erratic results obtained from preliminary investigations of LIX 64 and Adogen 283 suggested that fish mortality could have been induced by accidental contamination with the oily material, therefore, it was decided to limit LC_{50} determinations to the minnows only.

Dissolved oxygen concentrations of 36% and 38% saturation levels were encountered when testing LIX 64 and Adogen 283, however, oxygen levels for the rest of the chemicals tested never decreased below the 50% saturation level over the 96-hour exposure period.

Fathead minnows were significantly ($\rho < .01$) more sensitive to all the compounds tested.

The fish weight to volume relationship for minnows was .55 g/liter, being significantly greater ($\rho < .01$) than that for the guppies (.03 g/liter).

Surface area/volume ratios for the 8-liter and 10 liter test solutions were comparable at 1:6; and 1:57 respectively.

While toxicity evaluations of the final effluent provide the most accurate base for environmental impact assessment, the toxic unit concept as proposed by Sprague and Ramsay (1965) offers a useful tool for toxicity estimations.

A modification of the above concept utilizes the median lethal concentration (LC_{50}) for estimating effluent toxicities, by expressing the measured concentrations of each toxicant as a proportion of their respective LC_{50} values. Summation of these fractions provides a numerical value that can be used for ranking of effluent toxicities. The toxic unit concept is based on the premise that the final toxicity of a mixture of toxicants is equal to the sum of their individual toxicities. This hypothesis has been verified by numerous laboratory and field investigations (Herbert and Vandyke 1964; Jordan and Lloyd 1964; Brown et. al. 1969; Herbert 1965; Sprague et. al. 1965).

RECOMMENDATIONS

In the absence of more sophisticated criteria it is recommended that toxicities of mine-mill effluents be estimated by means of expressing the measured (or expected) concentrations of individual reagents as a proportion of their median lethal concentrations (LC_{50}). The numerical value obtained after addition of all the components of the effluent represent the toxicity of the whole effluent, and can be used for ranking purposes.

EXAMPLE:

$$\frac{\text{Actual Conc. of Compound "A"}}{LC_{50}\text{ in the same units}} + \frac{\text{Actual Conc. of Compound "B"}}{LC_{50}\text{ in the same units}} = \text{Toxic Unit of Effluent}$$

If the toxic unit value is greater than 0.1, bioassay testing of the whole effluent is warranted.

It should be understood, however, that a more rigorous evaluation is necessary in order to provide adequate protection for the more sensitive life-stages of the aquatic life. It is, therefore, suggested that for purposes of protecting the biota, concentrations of individual reagents in the effluent be limited to 1/10th of the LC_{50} values established herein. While this application factor is arbitrary, it is based on numerous lethal-sublethal relationships established experimentally (EPA 1975).

Table 1: List of Materials Tested

Trade Name	Major Constituent	Process Application
LIX 63	N.A.	Chelating Extractant
LIX 64	N.A.	Chelating Extractant
LIX 64N	N.A.	Chelating Extractant
LIX 70	N.A.	Chelating Extractant
Kelex 120	N.A.	Chelating Extractant
TBP	Tributyl Phosphate	Solvating Extractant
Isodecanol	Alcohol	Solvating Extractant
Dzehpa	Alkyl Phosphoric Acid	Liquid Cation Exchanger
Versatic 911	Carboxylic Acid	Liquid Anion Exchanger
Adogen 283	Carboxylic Acid	Liquid Anion Exchanger
Alamine 336	Carboxylic Acid	Liquid Anion Exchanger
Primene	Carboxylic Acid	Liquid Anion Exchanger
Aliquat 336	Quaternary Ammonium	Liquid Anion Exchanger

Table 2: Chemical Characteristics of the Experimental Water. (All values except conductivity expressed as milligrams per liter).

		Number of Analyses	Mean ± S.D.	Range
Hardness	$(CaCO_3)$	16	137 ± 3.87	130 - 142
Alkalinity	$(CaCO_3)$	16	89 ± 3.52	83 - 94
Chloride	(Cl^-)	16	33 ± 1.58	31 - 36
Free Ammonia	(NH_3)	16	.12 ± .05	.01 - .20
Nitrite	(NO_2)	16	.03 ± .01	.005 - .040
Nitrate	(NO_3)	16	.43 ± .19	.20 - .80
Sodium	(Na)	16	14 ± 1.23	13 - 17
Potassium	(K)	16	1.6 ± .23	1.2 - 2.1
Calcium	(Ca)	16	43 ± 1.44	40 - 45
Magnesium	(Mg)	16	7 ± 1.39	3 - 8
Sulphate	(SO_4)	16	31 ± 1.86	28 - 34
Conductivity	(micromhos)	16	339	330 - 360

Table 3: Results of Acute Toxicity Tests - all median lethal concentrations values expressed as mg/l.

	Fathead Minnows 96-hr. LC-50	Guppies 96-hr. LC-50
Dzehpa	135.0	173.0
Versatic 911	64.0	102.5
LlX 64	47.0	X
LlX 70	15.0	32.0
Adogen 283	9.7	X
TBP	9.6	18.0
Isodecanol	8.4	12.0
Alamine 336	4.0	10.0
LlX 64N	2.7	15.0
LlX 63	1.6	4.0
Kelex 120	.71	1.1
Primene	.27	.70
Aliquat 336	.14	.18

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